in the solution for unit mass of solvent added we get for the quantity dT∕c, where *c* is the concentration of the solution, the value 1·857° C. per unit concentration. Experimental measurements of freezing points of various non-electrolytic solutions have been made by Raoult, Loomis, Griffiths, Bedford and others and numbers ranging round 1∙85 found for this concentration. Equally good comparisons have been obtained for solutions in other solvents such as acetic acid 3∙88, formic acid 2∙84, benzene 5∙30, and nitro­benzene 6∙95. Such a concordance between theory and experi­ment not only verifies the accuracy of thermodynamic reasoning as applied to dilute solutions, but gives perhaps one of the most con­vincing experimental verifications of the general validity of thermo­dynamic theory which we possess.

Another verification may be obtained from the phenomena of vapour pressure. Since, in dilute solutions, the osmotic pressure has the gas value, we may apply the gas equation PV = nRT =*npv* to osmotic relations. Here *n* is the number of gramme-molecules of solute, T the absolute temperature, R the gas constant with its usual "gas.” value, *p* the vapour pressure of the solvent and v1 the volume in which one gramme-molecule of the vapour is confined.

In the vapour pressure equation *p-p' =Pσ/p,* we have the vapour density σ equal to M∕v1, where M is the molecular weight of the solvent. The density of the liquid is MN∕V, where N is the number of solvent molecules, and V the total volume of the liquid. Sub­stituting these values, we find that the relative lowering of vapour pressure in a very dilute solution is equal to the ratio of the numbers of solute and solvent molecules, or *(p — p')∣p =* *n*∕N.

The experiments of Raoult on solutions of organic bodies in water and on solutions of many substances in some dozen organic solvents have confirmed this result, and therefore the theoretical value of the osmotic pressure from which it was deduced.

Although even good membranes of copper ferrocyanide are rarely perfectly semi-permeable, and in other membranes such as india- rubber, &c., which have been used, the defects from the. theoretical values of the equilibrium pressure are very great, yet, in the light of the exact verification of theory given by the experiments described above, it. is evident that such failures to reach the limiting value in no wise invalidate the theory of osmotic equilibrium.. They merely show that, in the conditions of the particular experiments, the thermodynamic equilibrium value of the osmotic pressure cannot be reached—the thermodynamic or theoretical osmotic pressure (which must be independent of the nature of the membrane provided it is truly semi-permeable) is a different thing from the equilibrium pressure actually reached in a given experiment, which measures the balance of ingress and egress of solvent through an imperfect semi-permeable membrane.

Dilute solutions of substances such as cane-sugar, as we have seen, give experimental values for the connected osmotic properties—pressure, freezing point and vapour pressure—in conformity with the theoretical values. All these solutions are non-conductors of electricity. On the other hand, solution of mineral acids and salts conduct the current with chemical decomposition—they are called electrolytes. In order to explain the electrical properties of a solution, for instance of potassium chloride, we are driven to believe that each molecule of the salt is dissociated into two parts, potassium and chlorine, each associated with an electric charge equal in amount but opposite in sign. The movement in opposite directions of these charged ions constitutes the electric current in the solution. To explain the electrical properties of sulphuric acid in aqueous solution, the supposition of three ions, two of hydrogen and one of the chemical group SO4, is necessary. Now measurements of osmotic properties of these solutions show that their osmotic pressures are abnormally great and that, at extreme dilution, the ratio of their osmotic pressures to that of equivalent solutions of non-electrolytes is equal to the number of ions indicated by the electrolytic properties. From the osmotic side also, then, electrolytic dissociation is indicated, and indeed, it was from this side that the idea was first suggested by S. Arrhenius in 1887. The subject is dealt with in Electrolysis and Conduction, Electric: *§ In Liquids.*

*Concentrated Solutions.—*Having dealt with the relations between the properties of an ideally dilute solution, we now turn to the consideration of the general case where the simplifying assumption of great dilution is not made.

The height of the column of solution in fig. 13 required for osmotic equilibrium through a semi-permeable wall below is now very great, since the osmotic pressure of strong solutions may reach many hundred atmospheres. Hence we must not assume that the density of the vapour in the surrounding atmosphere is constant, or that the solution, when equilibrium is reached, is of uniform concentration throughout. The osmotic pressure (defined as the difference in the hydro­static pressures of the solution and solvent when their vapour pressures are equal and they are consequently in equilibrium through a perfect semi-permeable membrane) may also depend on the absolute values of the hydrostatic pressures, as may the vapour pressure of the liquids.

To investigate the osmotic pressure of a strong solution we may consider the hydrostatic pressure required to increase its vapour pressure to an equality with that of the solvent. The relation between hydrostatic pressure and the vapour pressure of a pure liquid may be obtained at once by considering the rise of liquid in a capillary tube. The difference in vapour pressure at the top and at the bottom of the column is *p — p' =Pσ/p,* as shown above for a column of solution. Writing *v* for 1∕σ, the specific volume of the vapour at the pressure *p,* and V for 1/p, the specific volume of the liquid at the pressure P, and restricting the result to small changes, we get *vdp=VdP.*

In considering the corresponding relation for a solution instead of a pure liquid, possible differences in concentration make the column method difficult of application, and it is better to attach the problem by means of an imaginary cycle of isothermal operation. The simplest way to do this is to imagine a vapour-sieve piston through which the vapour but not the liquid can pass. As we have explained above, such a vapour sieve may be constructed by boring a number of small enough holes through a solid not wetted by the liquid.

Let us imagine unit mass of solution of volume V confined in a cylinder ABC between a fixed vapour sieve B and a solid piston A by which a pressure P is applied. The vapour at pressure *p* in equilibrium with the liquid is bounded by a solid piston C, which we can also move to change the pressure or volume.

With such an imaginary apparatus, H. L. Callendar has shown that the variation of vapour pressure of a solution with pressure is given by the expression *V'dP=vdp,* where V' is the change in volume of the solution when unit mass of solvent is mixed with it. The. corresponding relation for a pure liquid can be regained by considering that at infinite dilution the liquid becomes pure solvent, and the change of volume becomes equal to the volume V of solvent added.

The osmotic pressure P0 is the difference of the hydrostatic pressures P' and P of the solution and the solvent when their vapour pressures arc equal. Hence dP0=dP'-*dP* and áPo/dP = (V—V')∕V' or dPo∕dP' = (V-V')∕V. If V=V' there is no. change in osmotic pressure with, hydrostatic pressure, and osmotic pressure depends on concentration and temperature only.

The relation between the equilibrium pressures P and P' for solution and solvent corresponding to the same value *po* of the vapour pressure is obtained by integrating the equation V'dP' = *vdp* between corresponding limits for solution and solvent. We get

*ΓP'V'dPf = ΓPo vdp* and fP WP = *p, vdp, J P' J P< J P J P*

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where *p* and *pf* are the vapour pressures of solvent and solution each under its own vapour pressure only.

If we measure the osmotic pressure Po when the solvent is under its own vapour pressure only, that is, when P ≡ *p = po,* the term involving V vanishes, and the limit of integration P' becomes P0+*p*. If we assume that V', the volume change on dilution, varies regularly or not appreciably with pressure, we may write the first integral as V'(Po÷∕>- *pf)* where V' now denotes its mean value between the limits.

To evaluate the second integrals *vdp* we may subtract a constant *b* to represent the defect of the volume of the vapour from the ideal volume *Rt∣p.* This gives

V'(Po+∕>-∕>')≈RZ log ⅛∕^)-5⅛-^).

For most experimental purposes the small terms involving the factor *(p-p')* may be neglected, and we have, approximately, P0V' = RMog⅛>∕∕>').

From this equation the osmotic pressure Po required to keep a solution in equilibrium as regards its vapour and through a